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Key Points:
- Degradation rates of DOC and composition of DOM from a peatland headwater stream
- Analysis showed relationship between composition and degradation rates
- Hydrology and aldehyde, carboxyl and N-alkyl functional groups showed to affect degradation rates

Supporting Information:
- Supporting Information S1

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Modeling rates of DOC degradation using DOM composition and hydroclimatic variables

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Abstract The fluvial fluxes of dissolved organic carbon (DOC) from peatlands form an important part of that ecosystem's carbon cycle, contributing approximately 35% of the overall peatland carbon budget. The in-stream processes acting on the DOC, such as photodegradation and biodegradation, can lead to DOC loss and thus contribute CO_2 to the atmosphere. The aim of this study was to understand what controls the rates of DOC degradation. Water samples from a headwater, peat-covered catchment, were collected over a 23 month period and analyzed for the DOC degradation rate and dissolved organic matter (DOM) composition in the context of hydroclimatic monitoring. Measures of DOM composition included ^{13}C solid-state nuclear magnetic resonance spectroscopy, bomb calorimetry, and elemental analysis. Regression analysis showed that there was a significant role for the composition of the DOM in controlling degradation with degradation rates significantly increasing with the proportion of aldehyde and carboxylic acid functional groups but decreasing with the proportion of N-alkyl functional groups. The highest rates of DOC degradation occurred when aldehyde functionality was at its greatest and this occurred on the recession limb of storm hydrographs. Including this knowledge into models of fluvial carbon fate for an 818 km^2 catchment gave an annual average DOC removal rate of 67% and 50% for total organic carbon, slightly lower than previously predicted. The compositional controls suggest that DOM is primarily being used as a ready energy source to the aquatic ecosystem rather than as a nutrient source.

1. Introduction

Northern Hemisphere peatlands cover only 3% of the Earth's land surface, but they store 20–30% of the terrestrial carbon (C) pool [*Gorham*, 1991]. In the UK, 15% of the land is covered in peatland, covering between 14,000 and 29,000 km^2 [*Tallis et al.*, 1997]; the majority of this peat is located in upland areas, where the higher altitude has allowed for the formation of deep blanket peats [*Evans and Warburton*, 2005]. As part of the carbon cycle within peatlands, the fluvial fluxes of carbon can represent 35% or more of the overall budget [*Worrall et al.*, 2003] and make the difference between a peatland being a net sink or source of carbon [*Billett et al.*, 2004]. The fluvial flux of carbon from a peatland includes particulate organic carbon (POC), dissolved inorganic carbon (DIC), and dissolved organic carbon (DOC) [*Dawson et al.*, 2004]. The dissolved organic carbon fraction is operationally defined as anything smaller than 0.45 μm, and the particulate fraction is anything larger than 0.45 μm [*Evans et al.*, 2005]. DOC is a component of dissolved organic matter (DOM), and approximately 50% of DOM is DOC. The terms DOM and DOC are often used interchangeably, but for this study, DOC refers to the concentration of the dissolved carbon, whereas DOM is the complex material that is predominantly carbon but also includes nitrogen, oxygen, hydrogen, and trace amounts of other elements. Similarly in this study, POC refers to the concentration of the particulate organic carbon, and particulate organic matter (POM) includes the carbon and other elements.

It is known that DOM can be highly labile and the processes that can act on DOM in peat sourced natural waters include flocculation [e.g., *McKnight et al.*, 1992], photodegradation [e.g., *Graneli et al.*, 1996], biodegradation [*Gregorich et al.*, 2003], release from POC (and therefore POM) [*Evans et al.*, 2012], in situ production [*Cole and Caraco*, 2001], and anthropogenic sources [*Kempe*, 1984]. The lability and reactivity of DOM means that it is important in a range of chemical processes in natural waters: the complexation and mobilization of heavy metals [*Aitkenhead et al.*, 1999], the regulation of pH [*Dawson et al.*, 2004], the availability of nutrients [*Qualls and Haines*, 1992], and an energy source for stream biota [*Bertilsson and Tranvik*, 1998]. Perhaps most importantly, the highly labile nature of DOM means that a large proportion of it is lost in transit through a river network and can contribute greenhouse gases to the atmosphere (CO_2, CH_4, and N_2O). Globally, *Cole et al.* [2007] estimated that 1.9 Pg C/yr enters rivers of which 0.8 Pg C/yr (42% of the input) is returned to the atmosphere. *Battin et al.* [2009] considered the loss of DOC from rivers at a global scale and suggested

21% removal of DOC in stream. *Regnier et al*. [2013] have estimated that the total carbon (inorganic and organic carbon) input to freshwaters was 2.8 Pg C/yr of which 1 Pg C/yr is exported from the tidal limit (i.e., a 64% removal rate). *Worrall et al*. [2016] considered not only the carbon but also the greenhouses gases that would result from the turnover of all fluvial carbon components (including DOM turnover to CO_2, CH_4, and N_2O) and found that DOM loss from UK rivers represented a flux to the atmosphere of 2.65 Tg C/yr (or 11.06 Tg CO_{2eq}/yr). Therefore, there is need to measure, assess, and understand the extent of DOM turnover in fluvial systems.

The extent of DOM removal will be critically dependent upon the rate at which DOM reacts and the time over which that reaction can take place. *Graneli et al*. [1996] found a rate of loss of 0.0009–0.4 mg C/L/d, and *Hudson et al*. [2003] found a DOC loss of 0.43%/d, both studies were in lake water. *Gennings et al*. [2001] state that 40–70% of annual inputs into boreal lakes were evaded to the atmosphere. Lakes and reservoirs have residence times of weeks to years, which are far longer than the residence times of rivers—median in-stream residence time for UK rivers is 26.7 h [*Worrall et al*., 2014]. *Worrall et al*. [2007] calculated a 29% removal rate of DOC over a 5 day period for UK rivers but for DOC at the river mouths as it entered estuaries when the DOM could already be considered "old." Several authors [*Marschner and Kalbitz*, 2003; *Southwell et al*., 2011] have expressed DOM turnover in terms of "young," readily biodegradable DOM, and old, refractory DOM. Therefore, in many studies it is the turnover of old refractory DOM that is being considered. *Dawson et al*. [2001] considered a short river reach of 2 km and found between 12 and 18% loss of DOC. *Moody et al*. [2013] found between 48 and 68% removal of DOC across an 818 km^2 catchment with a median residence time of 35 h. It is clear that if we are to understand the reactions of DOM and DOC, we need to understand reactions of the freshest material, i.e., the DOM as it leaves the soil for the fluvial network. *Worrall and Moody* [2014] proposed rate equations for the turnover of fluvial organic carbon (DOC and POC) and used these rate laws to estimate losses across national scale catchments but the estimation was limited by not knowing what rate constants were appropriate, i.e., rate laws and rate orders were known but the study had no way of knowing what rate constants were appropriate for which conditions and as such, the rate constants had to be chosen stochastically from a distribution of empirical values. If we are to understand DOM lability and release to the atmosphere, then we need a way of understanding, and predicting, the rates of turnover. Therefore, we propose that we can understand rates of DOM turnover from the composition of the DOM and that the composition and character of the DOM, and therefore turnover, can be predicted from prevailing hydroclimatic conditions which are themselves readily predicted from physical models.

The name "DOM" is a widely used, rarely defined term, often described as comprising of organic compounds such as fulvic and humic acids in various states of degradation [*Thurman*, 1985] and the composition of the DOM is thought to affect the rates of photodegradation and biodegradation of the matter [*Amon and Benner*, 1996]. Studies have attempted to classify the exact composition and character of DOM, using various analytical techniques, including ^{13}C nuclear magnetic resonance (NMR) [e.g., *Abdulla et al*., 2010b; *Wetzel et al*., 1995], thermal analysis [e.g., *Peuravuori et al*., 1999; *Plante et al*., 2009], and elemental analysis [e.g., *Provenzano and Senesi*, 1999; *Worrall et al*., 2013]. Fewer studies have explored the link between DOM composition and its behavior in aquatic environments. *Kulovaara et al*. [1996] and *Sachse et al*. [2005] have both suggested that the labile pool of DOM is composed of low molecular weight carbohydrates, amino acids, peptides, small carboxylic acids and alcohols, whereas *Tranvik et al*. [2009] have associated the refractory component with higher molecular weights, more aromatic in character, and composed of lignin and humic compounds: the two components can be broadly separated by molecular weight [e.g., *Abdulla et al*., 2010a; *Amon and Benner*, 1996]. *Baldock et al*. [2004] used ^{13}C NMR to model the composition of soil organic matter and explain biochemical recalcitrance and decomposition rates in soil. However, understanding the link between composition and degradation will be more useful if we can predict compositional changes and degradational changes in source waters. Therefore, the aim of this study was to investigate the influence of DOM composition and changes in hydroclimatic conditions on the rate of degradation of DOC (via both bio- and photo-induced degradation) in an upland, peat-sourced headwater.

2. Approach and Methodology

The approach taken by this study was to measure the degradation of DOC within the fluvial network of a peat-covered catchment where the hydroclimatic context was known. Water samples were taken from

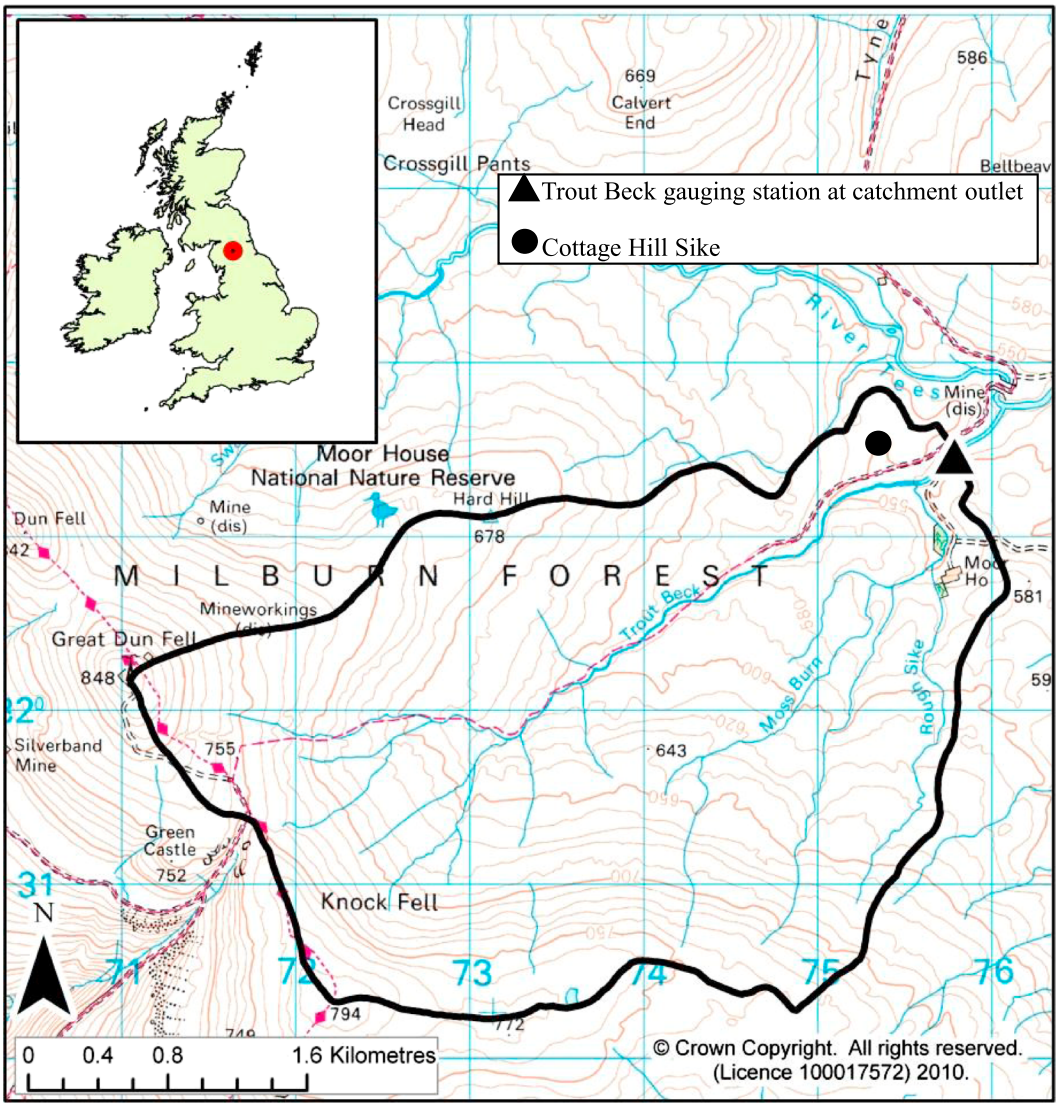

Figure 1. Map showing the location of the Trout Beck catchment at Moor House NNR and the sampling location of Cottage Hill Sike.

Cottage Hill Sike, a first-order, peat-covered stream catchment in river Tees catchment, and within Moor House National Nature Reserve (NNR, Figure 1, UK national grid ref. NY 756326). The water was sampled monthly over the course of 2.5 years (except when poor weather conditions prevented access to Moor House NNR) so that, a priori, water samples were taken across a range of both meteorological and hydrological conditions, DOC concentrations, and DOM compositions. Water was taken from Cottage Hill Sike from October 2011 to January 2014, resulting in 23 DOM solid samples with a full range of analyses carried out and 17 monthly degradation experiments. Moor House NNR and Cottage Hill Sike have been extensively used in several similar studies [*Garnett et al*., 2001; *Moody and Worrall*, 2016].

2.1. Study Site

The study site lies within Moor House NNR, a terrestrial and freshwater site which is part of the UK Environmental Change Network (ECN). The underlying geology is a succession of Carboniferous limestones, sands, and shales with intrusions of the doleritic Whin Sill [*Johnson and Dunham*, 1963]. This solid geology is covered by glacial till whose poor drainage facilitated the development of blanket peat during the Holocene. Blanket peat covers 100% of the Cottage Hill Sike. The vegetation is dominated by *Eriophorum* sp. (cotton

grass), *Calluna vulgaris* (heather), and *Sphagnum* sp. (moss). None of the catchment area has experienced prescribed burning or wildfire since 1954 [*Garnett et al*., 2001].

An ECN automatic weather station at the site records the hourly solar and net radiation; air temperature, wind speed and direction, rainfall, sky and ground albedo, and soil temperature. From 1993 to 2013, the average air temperature was 5.9°C (range −16.8–27.6°C) and the mean annual precipitation was 1930.9 mm (range 869.2–2763.4 mm). For the same time period (1993–2013), Cottage Hill Sike river water had a median conductivity of 42.94 μS/cm, pH of 4.36, and DOC concentration of 18.1 mg C/L. The UK Environmental Change Network has recorded the river discharge of Trout Beck, the catchment outlet, every 15 min, since 1993.

2.2. Hydroclimatic Variables

The ECN records [*Rennie et al*., 2015a] were used to calculate the average flow at Trout Beck on each sampling occasion, for the exact hour of sampling, for each hour on the day of sampling, and the preceding 6 days. The flow on the sampling day was calculated per hour, resulting in the average flow for each of the previous 24 h, and for the each day for the whole week before the water samples were taken. The air and soil temperature (at 10 and 30 cm depths) and rainfall data from the ECN weather station [*Rennie et al*., 2015b] were treated in the same way as the discharge data, resulting in a data set of the average temperature and rain for the preceding 6 days and each hour of the preceding 24 h. The rainfall data were also summed over each day and hour, so the total rainfall could also be considered, but this was not significant in any model, so not considered further.

The daily air and soil temperatures, rainfall, and river discharge on sampling days fell within the 5th to 95th percentiles of all daily values from October 2011 to January 2014 except on one occasion in July 2013 when the air and soil temperature exceeded the 95th percentile and the discharge and rain fell below the 5th percentile. The sampling day data will be slightly skewed as bad weather sometimes prevented access to Moor House NNR, and so coldest extremes may not be well represented; however, the air temperature was in the bottom 10th percentile on two occasions and both of these were in winter months.

2.3. Initial Water Chemistry

For any sampled water the initial water chemistry measurements were made for pH, conductivity, absorbance at 400 nm, suspended sediment concentration, and DOC concentration of the river water. For all analyses except suspended sediment concentration, the water was syringe filtered to 0.45 μm, and then the conductivity and pH were measured using electrodes; the absorbance at 400 nm was measured using an UV-Vis spectrophotometer (Jenway 6500), with a 1 cm cuvette; the DOC concentration (not the DOM concentration) was measured using the wet oxidation method described in *Bartlett and Ross* [1988]. The DOC concentrations were calibrated using standards of oxalic acid with known concentrations, and only calibration curves with an r^2 of 0.95 or above were used. Samples for DOC analysis were "fixed" at the streamside using concentrated sulphuric acid to remove inorganic carbon and prevent further changes in DOC concentration before completion of the analysis in the laboratory. Sulphuric acid was used as its addition is the first step in the Bartlett and Ross procedure. The detection limit for this method was assessed as being 0.5 mg C/L, and all results were analyzed as part of a statistical experimental design which allowed any experimental effect to be judged relative to measurement error.

For suspended sediment concentration samples were filtered through preweighed, 0.5 μm, glass fiber filters, dried to 105°C and the filter paper reweighed to give the concentration of suspended sediment. The filter papers were then put in a furnace for 4 h at 550°C and then reweighed. The mass lost in the furnace equates to the mass of POM, and based upon previous analysis of POM samples from this catchment, 47.5% of this was assumed to be POC [*Moody et al*., 2013].

2.4. DOC Degradation

A subsample of the sampled water was used to determine the DOC degradation rate, using a similar method as *Moody and Worrall* [2016]. The unfiltered river water was kept outside in natural light and temperature conditions, in quartz glass tubes. The glass tubes were approximately half-full of water, with an air headspace, stoppered with a rubber bung at the bottom and loosely stoppered at the top. The quartz glass tubes, which allow all wavelengths of solar irradiance at the Earth's surface to pass through, had a diameter 55 mm and

were filled to give a water depth of approximately 150 mm. An examination of the flow stage records for the sample stream showed that 150 mm was the 46.5th percentile flow depth, i.e., 150 mm represented almost median flow depth in the source stream. Light attenuation can be considerable in colored waters, and *Bukaveckas and Robbins-Forbes* [2000] have related light attenuation to DOC in 85 Adirondack lakes. Taking the best fit equation from *Bukaveckas and Robbins-Forbes* [2000], the half-depth of light attenuation could be calculated for Cottage Hill Sike. For the measured DOC concentrations (1993–2010) the interquartile range of half-depth of light attenuation was 150 to 340 mm, i.e., the quartz tubes represented 100% of the light penetration 25% of time but 62.5% of the light penetration 75% of the time. Furthermore, at the tidal limit of the study catchment (only a median water transit time of 35 h from Cottage Hill Sike) [*Worrall et al*., 2014] the half-depth of light attenuation has an interquartile range of 62 to 102 mm but examining the flow stage duration for the tidal limit shows that even 62 mm water depth was only exceeded on 17% of days and 102 mm was exceeded on only 7% of days, i.e., there was almost full light penetration most of the time. Of course, such a light penetration calculation estimates the light conditions experienced by the base of the quartz tube while DOC molecules will move up and down the water column in the quartz tube on convective currents and so experience a range of light conditions greater than those estimated above. The attenuation was assessed at 300, 340, and 440 nm on the basis that this would cover UV-B, UV-A and photosynthetically active radiation (PAR). In keeping the depth of the water in the quartz glass tubes similar to the depth of the stream, hopefully, the effects of UV-light toxicity on the microbiology was minimized [*Kramer and Ames*, 1987].

Half the water samples in glass tubes were exposed to ambient light conditions (i.e., experiencing a diurnal cycle in daylight and air temperature: ambient treatment), and half of the samples in glass tubes were wrapped in foil to be kept in the dark (dark treatment) so that they only experienced a diurnal cycle in air temperature. These treatments were used so as to distinguish between the photo-mediated and non-photo-mediated components of the degradation, and the difference between ambient and dark DOC concentration change was considered the photo-induced DOC change. Photo-induced degradation includes any potential priming of microbial heterotrophs due to the release of photosynthetic compounds in the ambient treatment. Note that the samples were not filtered prior to the experiment, which meant that both DOM and POM were present in the quartz glass tubes; this approach meant that both production and degradation of DOC and POC and the interchange between them were possible, as well as microbial processes—many studies [e.g.s, *Stutter et al*., 2013] have filtered and therefore removed the POM and focused on only on DOM, but this would never occur in natural waters. The method used here resulted in three rates: ambient rate (from the ambient treatment), dark rate (from the dark treatment), and photo-induced rate (assumed as the difference between ambient and dark treatments). A data logger with a PAR (photosynthetically active radiation) meter and thermocouple recorded the radiation levels and air temperature at 15 min intervals throughout the time of each month's experiment.

These experiments were carried out monthly for approximately 70 h, an entire quartz glass tube of approximately 350 mL water sacrificially sampled at frequent intervals throughout. During the first daylight period of the experiment, samples were taken at hour 1, 2, 4, and then at dusk. Samples were then taken at subsequent dawns and dusks. Fixed numbers of hours since the start of the experiments were not used because changes in the initial river sampling time and changes in day length over the year would mean that samples taken in daylight 1 month could be in darkness in subsequent months. All water samples taken were analyzed by the same method as the initial water samples, outlined above. Replicates were included as often as equipment availability allowed, and 124 of 310 water samples were replicates (40%), evenly distributed over the different time points over the course of the experiments. The experiment was carried out beside the stream at the field site for the first day, then the samples were moved to outside the laboratory after dark where the rest of the experiment was conducted. The PAR and air temperature recorded and used in subsequent models reflect those experienced by the samples, even including the journey from the field to the lab, rather than constantly using the PAR and temperature of the field site.

2.5. DOM Characterization

For DOM characterization this study used the approach of *Worrall et al*. [2015], which had already been applied in the study catchment. A large volume sample (at least 22 L) was returned to the laboratory on the day of collection, but unlike the samples for DOC analysis in the degradation experiments described

above there was not the time constraint on processing these large samples and so filtering was not used but the sample was allowed to settle so as to separate the particulate from the truly dissolved or colloidal. This method did not result in pure DOC, as the dissolved and colloidal material contained more than just carbon, so was not considered to be measuring exactly the same component of the water as the DOC analysis on the filtered water as described above. The DOM collected via this method was compared to the DOC concentrations of the water and used to explain the degradation but was not assumed to be the same as the DOC measured via filtering and subsequent analysis. Filtering the water applies a very strict size constraint on the organic matter molecules, and for this study of the composition of the organic matter, it was deemed more suited to allow separation via settling rather than filtering.

The supernatant was tapped off above the deposited layer of particulate material and the supernatant was evaporated to dryness at 80°C and the residue collected for analysis. On average it took 9.8 days to evaporate approximately 20 L of water, and as a means of testing for change in concentration of the processing a water sample was taken for analysis from the last portion of supernatant to be put into the evaporating dish. The DOC concentration in this supernatant water was compared to the initial DOC concentration of the water at sampling to test for any changes during the days, while the water was in the laboratory. The difference between these two concentrations was tested by *t* test to assess for any significant change.

The temperature of 80°C was chosen as warm enough to facilitate relatively quick evaporation of the supernatant water, but not so hot as to alter the composition of the DOM. Several studies have looked at the weight loss, thermal stability, and composition of soils and organic matters exposed to heat and thermogravimetric analysis and concluded that under 100°C the only weight loss was water. *Kolokassidou et al*. [2007] analyzed humic acids heated to different temperatures (40 to 110°C) using mass spectrometry and found that the 5.5% of the sample weight was lost between 60 and 100°C was water, and *Lopez-Capel et al*. [2005] concluded that an endothermic peak between 62 and 91°C was dehydration. Some studies did not consider the weight loss below 125°C [*Bergner and Albano*, 1993], or even 105°C [*Peuravuori et al*., 1999], and a review by *Plante et al*. [2009] focuses on temperatures greater than 100°C. These studies all use thermogravimetric analysis as a method for determining characteristics or structure of organic matter, suggesting that heating organic matter to higher temperatures than used in this study is not an impediment to investigating the characteristics or structure of organic matter. Also, it was assumed as all samples were heated to the same temperature, if there were an effect of the temperature on the structure of the molecules or the mass of the compound would be consistent across all samples.

The supernatant water was not filtered so as not to impose a "size" constraint on the DOM being sampled and so the DOM sampled was by definition colloidal. Various studies have imposed different constraints on the size of particles that constitute DOM, such as 0.1 μm [*Abdulla et al*., 2010a; *Hertkorn et al*., 2006], 0.2 μm [*Kalbitz et al*., 2003], and 0.6 μm [*Amon and Benner*, 1996].

The process of generating solid samples of DOM was designed to provide sufficient sample for subsequent analysis: typically 0.8 to 1 g of DOM. The samples were not recovered quantitatively and so precise yields cannot be known, however, given that typical initial stream water was of the order of 40 mg C/L, that 20 L of stream water was evaporated, and that DOM is typically 40 to 50% C then a minimum yield of 60% was being achieved.

The suspended material that sank to the bottom of the sample was not added to the evaporation dish and excluded from the subsequent DOM analysis. The residue of the evaporation was collected as dried powder; due to the low ash content of the DOM collected by this method (as confirmed by thermogravimetric analysis and elemental analysis), no further sample preparation was needed before analysis. The DOM samples were analyzed for their energy content (bomb calorimetry), elemental composition (elemental analysis), and relative functional group composition (^{13}C NMR). For comparison to the DOM samples, standards of cellulose and lignin were analyzed in the same way as the samples; however, these were not exposed to the same heat as the DOM samples were during collection. The lignin was sourced from Sigma-Aldrich and the cellulose from Whatman. The samples were also subject to thermogravimetric analysis, inductively coupled plasma optical emission spectroscopy, pyrolysis gas chromatography mass spectroscopy, Fourier transform infrared spectroscopy, and stable isotope analysis (^{13}C and ^{15}N); however, the results of these analyses were not statistically significant in any models and so are not considered further here.

2.5.1. Bomb Calorimetry

Bomb calorimetry was used to measure the energy content (gross heat value) of materials ($MJ\ kg^{-1}$), by measuring the temperature change in the water surrounding the "bomb". Energy contents were used to infer information about the structure of the samples [e.g., *Masiello et al*., 2008]. The bomb calorimetry was carried out using a Parr 6200 calorimeter with an 1108 Oxygen Bomb, with a Parr 6510 water handling system, which is precise to 0.1%. Approximately, 250 mg of each solid was used, "spiked" with 750 mg of benzoic acid to increase the mass to approximately 1 g. Benzoic acid standards were also used to calibrate the machine.

2.5.2. Elemental Analysis

The elemental analysis was carried out for carbon, hydrogen, nitrogen, and oxygen content of the DOM using a Costech elemental combustion system with pneumatic autosampler. Between 1.5 and 2.5 mg of each sample was used, packed in 5 × 3.5 mm tin capsules. The samples were analyzed in triplicate for carbon, hydrogen, and nitrogen and separately for oxygen. Samples with a relative standard error of more than 5% were reanalyzed. Standards of acetanilide (C_8H_9NO) were used to calibrate the machine. Only calibrations with a linear regression r^2 of 0.999 were used in calculations.

For the CHN combustion analysis, the reaction column contained chromium (III) oxide, copper wires and silvered cobaltous-cobaltic oxide and was heated to 1000°C. The carrier gas was helium at a flow rate of 140 mL/min; the oxygen flow rate was 40 mL/min. The oxygen gas reacted with the tin capsule and sample at high temperatures (1700–1800°C). The GC column (at 60°C) was stainless steel, 2 m length, packed with porapak QS used to separate the gases. A thermal conductivity detector was used to calculate the signal of each sample.

For the oxygen pyrolysis analysis, the reaction column contained 20% nickelized carbon and silica chips and was heated to 1060°C. The carrier gas was helium at a flow rate of 140 L/min. A water trap of magnesium perchlorate ($Mg(ClO_4)_2$) was used to remove any water from the system. The GC column (at 60°C) was a stainless steel, 1 m in length, molecular sieve column. The samples were doped with chloropentane ($C_5H_{11}Cl$) to aid combustion and enhance the catalytic effect of the nickelized carbon (by removing the nickel as nickel chloride and exposing a renewed nickel/carbon interface to the pyrolysed gases).

Molar proportions of the four measured elements were calculated from ash corrected data assuming 2% for missing elements sulphur and phosphorus. From the molar concentrations the carbon oxidation state (C_{ox}) [*Masiello et al*., 2008], the oxidative ratio (OR) [*Masiello et al*., 2008], the degree of unsaturation (Ω) and the C:N, O:C, and H:C ratio of the samples were calculated. The degree of unsaturation, which varies between 4 for benzene and 0 for a pure alkane and is a measure of the number of rings and p bonds within a molecule, is defined as follows:

$$\Omega = [C] - \frac{[H]}{2} - \frac{[N]}{2} + 1. \quad (1)$$

2.5.3. ^{13}C Solid-State Nuclear Magnetic Resonance (^{13}C-NMR)

The ^{13}C solid-state NMR was used to identify the main functional groups of the samples. The data were obtained at the Engineering and Physical Sciences Research Council UK National Solid-state NMR Service at Durham University. Solid-state ^{13}C NMR spectra were recorded at 100.56 MHz using a Varian nuclear magnetic resonance spectrometer and a 4 mm magic-angle spinning probe. They were obtained using cross polarization with a 0.5 s recycle delay, 1 ms contact time, at ambient probe temperature (~25°C) and at a sample spin rate of 14 kHz. Between 50,000 and 100,000 repetitions were accumulated. Spectral referencing was with respect to an external sample of neat tetramethylsilane (carried out by setting the high-frequency signal from adamantane to 38.5 ppm). Between 50 and 60 mg of each sample was used in this analysis. The chemical shift ranges used were taken from *Chadwick et al*. [2004] and are shown in Table 1 and Figure 2 and are as used by *Baldock and Skjemstad* [2000] to describe the degradation process of organic matter. The maximum peak height in each range was divided by the percentage carbon content (from the elemental analysis) to get a relative peak height for each type of carbon observed. The proportion of the total carbon that was attributed to each functional group was also calculated.

2.6. Statistical Methodology

Analysis was focused upon the initial rates within the first hour of the experiment, as previous studies [*Moody et al*., 2013] have shown that the majority of degradation takes place in the first day and especially the first

Table 1. The Ranges of Chemical Shifts for ^{13}C NMR, From *Chadwick Et Al.* [2004], and the Proportion of Each Carbon Type in Each DOM Sample

Sample			Chemical Shift (ppm)							
			0–45	45–65	65–95	95–110	110–145	145–160	160–190	190–220
Year	Month	Rep	C-Alkyl	N-Alkyl	O-Alkyl	O_2-Alkyl	Aromatic	Phenolic-C	Carboxyl-C	Aldehyde-C
2011	10	1	13.70	7.74	12.24	10.52	12.86	10.64	25.10	7.20
2011	11	1	16.73	15.71	23.54	7.48	8.56	4.94	18.60	4.43
2012	2	1	21.25	7.87	10.81	8.03	8.48	7.05	25.50	11.00
2012	3	1	15.72	9.04	14.89	11.29	13.22	9.49	21.01	5.34
2012	4	1	11.70	8.93	15.03	12.05	13.06	10.49	23.49	5.26
2012	5	1	16.95	14.85	20.23	11.68	15.71	7.91	9.68	2.98
2012	6	1	14.12	13.25	12.27	10.92	12.85	9.61	21.98	5.00
2012	7	1	9.88	9.81	11.85	13.73	15.98	15.31	16.25	7.19
2012	7	2	10.47	10.22	19.21	11.09	12.35	9.23	22.71	4.72
2012	8	1	11.84	11.22	19.65	12.90	12.13	9.46	18.84	3.97
2012	9	1	14.58	10.69	16.67	11.18	13.60	10.60	18.76	3.93
2012	10	1	15.82	10.27	16.13	11.95	12.41	10.49	18.20	4.74
2012	11	1	17.57	8.98	10.50	9.47	9.81	8.44	26.14	9.08
2013	1	1	17.16	8.53	12.44	9.02	11.08	8.35	26.09	7.34
2013	3	1	19.63	7.63	9.60	9.33	11.72	9.61	24.48	8.00
2013	4	1	23.09	8.01	11.72	8.19	9.78	7.03	23.77	8.42
2013	5	1	12.64	7.25	8.01	10.13	13.56	11.66	27.05	9.72
2013	6	1	11.56	7.82	9.23	11.21	12.93	11.30	26.72	9.23
2013	7	1	16.00	8.76	9.40	8.64	11.63	9.31	26.13	10.14
2013	8	1	10.04	7.12	6.32	10.92	15.71	13.52	26.54	9.82
2013	9	1	10.59	7.73	8.91	11.36	12.42	11.26	29.41	8.31
2013	12	1	12.42	8.53	11.44	10.88	12.00	10.35	25.81	8.57
2014	1	1	14.77	8.22	10.96	9.87	12.21	10.65	24.10	9.22
Mean			14.71	9.49	13.09	10.51	12.35	9.86	22.88	7.11
Maximum			23.09	15.71	23.54	13.73	15.98	15.31	29.41	11.00
Minimum			9.88	7.12	6.32	7.48	8.48	4.94	9.68	2.98

period of daylight. Rates of DOC concentration change were calculated for the three treatments (ambient, dark, and photo-induced rates) for each month's degradation experiment. Where necessary the rate of change was calculated for the whole first day then divided by 24 to get the hourly rate.

Analysis of variance (ANOVA) was used to assess differences between treatments (ambient, dark, and photo-induced rates) and between months and was applied to rate and compositional data. Changes in DOC concentration and DOM composition were assessed by one-way ANOVAs with only the differences between months as a factor. Prior to ANOVA all data were tested for homogeneity of variance and normality using the Levene and Anderson and Darling tests, respectively. If either test were failed, then the data were log-transformed and retested; no further transformation was found to be necessary.

Initial rate analysis was used to assess the order of the reaction. Subsequently, regression analysis was used to compare the rate of DOC changes in the three different treatments (ambient, dark, and photo induced) to the compositional DOM data (elemental and relative functional group composition; C_{ox}, OR, and Ω; gross heat), water chemistry, environmental variables (PAR and experiment air temperature), and hydroclimatic variables data from the ECN monitoring. In this regression analysis the specific rate was used (i.e., $\frac{\text{rate}}{[DOC_0]}$), where $[DOC_0]$ is the initial DOC concentration in each set of rate experiments. The hourly hydroclimatic data (air and soil temperature, discharge, and

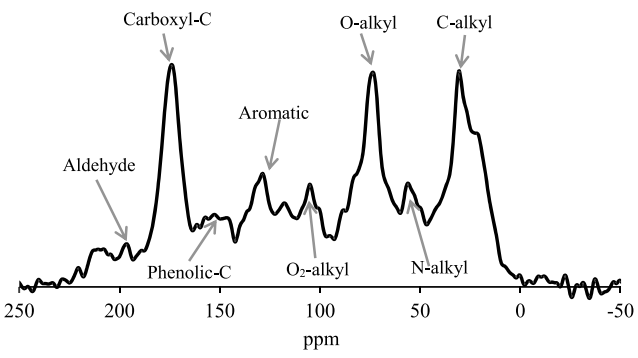

Figure 2. An example ^{13}C NMR spectrum of one DOM sample, with the carbon functional group ranges labeled.

Table 2. The Range and Median Values of the Elemental Compositional and Energy Content of the DOM, the Change in the DOC Concentration in the Ambient and Dark Treatments, and the Photo-Induced Change in DOC Concentration During the First Hour of the Degradation Experiments

Variable	Minimum	Maximum	Median
Gross heat (*MJ* kg^{-1})	4.9	14.0	11.8
Carbon (mol/100 g)	3.02	4.09	3.77
Hydrogen (mol/100 g)	3.73	5.86	4.50
Oxygen (mol/100 g)	2.64	3.30	2.90
Nitrogen (mol/100 g)	0.08	0.18	0.13
C:N	17.87	44.91	29.67
H:C	0.98	1.94	1.21
O:C	0.65	1.09	0.77
Carbon oxidation state (C_{ox})	0.28	0.65	0.42
Degree of unsaturation (Ω)	1.04	2.89	2.43
Oxidative ratio (OR)	0.86	0.96	0.92
Ambient treatment DOC concentration change (mg C/L)	−5.27	37.05	10.28
Dark treatment DOC concentration change (mg C/L)	−5.10	7.66	0.45
Photo-induced DOC concentration change (mg C/L)	−3.23	36.46	3.14

rainfall) were considered as the current at time of sampling and for each of the 24 h prior to sampling. All variables were considered as measured and log-transformed as were the rate values. In addition, the temperature during the experiment was transformed as the reciprocal of the absolute temperature so as to test for the activation energy of the reaction. Similarly, the month factor was included as continuous variable by transformation into the sinusoidal function: $\left(\sin\left(\frac{m\pi}{6}\right)+\cos\left(\frac{m\pi}{6}\right)\right)$, where m is the month number (January = 1 to December = 12). Stepwise regression analysis was used with forward and backward selection and a probability of being zero of 5% being used as the criteria for inclusion. The variance inflation factor (VIF) was used to check for colinearity between variables selected within the stepwise regression, VIF $>$ 5 was considered indicative of collinearity, and variables were removed.

2.7. Model Application

The results of the above assessments of controls upon rate laws were applied to the model as developed in *Worrall and Moody* [2014]. All model parameters and inputs were maintained as in the application of *Worrall and Moody* [2014] except that the selection of rate constants was no longer stochastic. The previous prediction of DOC and POC removal were then compared to those based upon results of this study.

3. Results

The results of the NMR, bomb calorimetry, and elemental analysis on the DOM samples are shown in Tables 1 and 2 and Figure 3. The DOC concentrations in the initial water samples ([DOC_0]), taken directly from the river, ranged from 23.7 to 96.5 mg C/L with a mean and standard error of 40 ± 4 mg C/L (Figure 3). The POC concentrations ranged from 1.85 to 7.03 mg C/L with a mean of 3.8 ± 0.5 mg C/L (Figure 3). There were no significant differences between the different months for either the initial DOC concentration (p = 0.7663) or the initial POC concentration (p = 0.3568).

The analysis of the supernatant water showed that in the average of 9.8 days it was stored in the laboratory, the DOC concentration increased from of an initial average of 40 mg C/L to 45 mg C/L; although a t test showed that there was no significant difference in the DOC concentration between the initial stream water and the final settled water. This slight, but insignificant, increase may be attributable to the water not being filtered, allowing microbes to degrade DOC and POC to convert to DOC (and vice versa), but equally, this lack of significant difference could be due to the sample being stored in the dark while settling.

3.1. DOM Characterization

3.1.1. Bomb Calorimetry

The median monthly gross heat value was 11.76 *MJ* kg^{-1}, and ranged from 4.92 to 13.96 *MJ* kg^{-1} (Figure 3); an ANOVA on the data showed that there was no significant difference between the months (p = 0.4611). The cellulose and lignin standards had gross heat values of 16.62 and 25.44 *MJ* kg^{-1}, respectively.

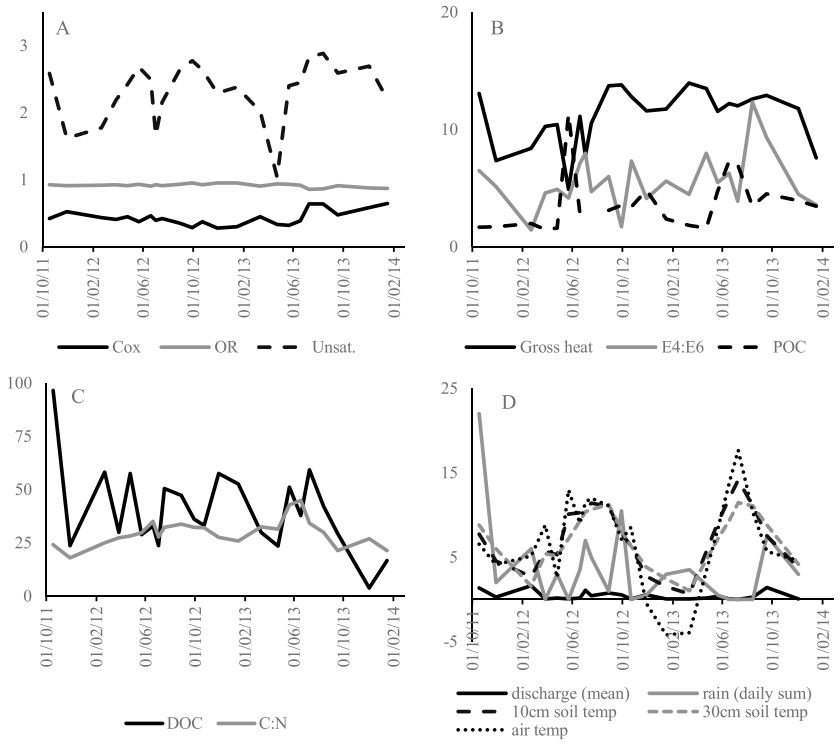

Figure 3. The variation in the carbon quality and quantity over time; (a) the carbon oxidation state (C_{ox}), oxidative ratio (OR) and degree of unsaturation (unsat.) of the DOM; (b) the gross heat of the DOM (*MJ* kg^{-1}), E4:E6 ratio, and POC concentration (mg C/L) of the initial water samples; (c) the C:N ratio of the DOM and DOC concentration of the initial water samples (mg C/L); and (d) the mean discharge (m^3/s), total rainfall (mm), mean soil temperature (at 10 and 30 cm; °C), and mean air temperature (°C) on the sampling day.

3.1.2. Elemental Analysis

The mean (±standard error) percentage content of carbon, hydrogen, oxygen, and nitrogen were 44.32 ± 0.64%, 4.61 ± 0.10%, 46.59 ± 0.51%, and 1.80 ± 0.08%, respectively (Table 2). The mean average molecular formula, proportionate to 100 mol of carbon, of the DOM was $C_{100}H_{125}O_{79}N_{3.5}$.

The values of C_{ox} and OR are, by definition, closely and negatively correlated. For the samples of DOM from this study the C_{ox} varied from 0.28 to 0.65 leading to OR values between 0.86 and 0.96 (Table 2 and Figure 3). The measured standards of cellulose and lignin had OR values of 0.99 and 1.12, respectively, and the ideal photosynthetic process would by definition have an OR of 1.

The degree of unsaturation can range from 0 for a pure alkane, with the formula C_nH_{2n+2}, to 4 for benzene, where there are an equal number of carbon and hydrogen atoms. The degree of unsaturation of the DOM samples ranged from 1.04 to 2.89, suggesting that the samples are partially saturated. For comparison, the cellulose and lignin values were 1.47 and 3.09, respectively.

There was no seasonal cycle to the elemental composition data, or the ratios, and therefore also for the C_{ox}, OR, and degree of saturation, and ANOVA on these data showed that there were no significant differences between the months for any variable.

3.1.3. ^{13}C Solid-State Nuclear Magnetic Resonance (^{13}C-NMR)

There were 23 DOM samples analyzed by NMR, two from each calendar month, except February and December, which had 1 sample each, and July, which had three samples. An example spectrum is shown in Figure 2. The peak in the carboxyl-C region of the spectra was highest for all samples, suggesting that all samples contained a large proportion of COOH groups. Proportionally, if DOM was composed of 100 carbon atoms, on average there would be 15 C-alkyl, 9 N-alkyl, 13 O-alkyl, 11 O_2-alkyl, 12 aromatic, 10 phenolic, 7 aldehydes, and 23 carboxyl groups (Table 1). An ANOVA on the NMR data showed no significant differences between the months for each of the eight ranges, and no seasonal pattern was observed.

3.2. DOC Degradation

The DOC concentration change during the first hour of the experiment ranged from +5.27 to −37.05 mg C/L in the ambient (median −10.28 mg C/L; Table 2) and +5.10 to −7.63 mg C/L in the dark treatment (median −0.45 mg C/L; Table 2). Net DOC production occurred in 1 month in the ambient and in 5 months in the dark treatment. There were no significant differences in the DOC degradation rates between months for either the ambient (p = 0.2559) or dark (p = 0.0508) treatments. In general, there were higher DOC concentration changes (DOC loss) in the dark treatment in the summer months. There were significant differences between the ambient rates and the dark rates (p = 0.0013) with the dark rates being significantly lower than the ambient rates. In the ambient treatment, on average (±standard error) 28.79 ± 2.81 mg C/L was lost over the 70 h of the experiments, at a rate of −0.46 ± 0.05 mg C/L; this was an average 68 ± 5% loss. The specific rates of degradation (initial rate/initial DOC concentration) varied from −0.18 to 0.64 per hour in the ambient treatment and from −0.17 to 0.16 per hour in the dark treatment; again, there were no obvious seasonal cycle.

From the DOC concentration change in the ambient and dark treatments in the first hour of the experiment, the initial photo-induced rate of DOC change was estimated to range from +3.23 to −36.46 mg C/L (median −3.14 mg C/L; Table 2). In 4 months the DOC loss in the dark treatment during the first hour of the experiment was greater than the DOC loss in the ambient treatment. There were no significant differences in the photo-induced rates between months (p = 0.1937).

As the water used in the degradation experiments was not filtered, these reflect the net changes in DOC concentration, so potentially include production of DOC from POC in addition to loss of DOC via degradation.

3.3. Modeling DOC Concentration Change

The initial rate (rate of DOC loss in the first hour of the experiment) analysis for the ambient treatment rates gave the following:

$$\underset{(0.84)}{\log_e(\text{rate})} = \underset{(3.2)}{2.3\log_e[\text{DOC}_0]} - 6.5 \qquad n = 16, r^2 = 0.33, \tag{2}$$

where $[\text{DOC}_0]$ is the initial DOC concentration in each experiment with the values in brackets below the equation representing the standard error in the coefficient and constant terms. This method of analysis would suggest that at Cottage Hill Sike in the light, the initial reaction is of the order 2.3 ± 0.8 which is not significantly different from either second or third order. However, it is most likely to be fractional or mixed order because of the number of potential processes contributing.

When compositional data were considered relative to the specific rate, then only very few variables proved to be significant and the best fit model becomes

$$\log_e\left(\frac{\text{rate}}{[\text{DOC}_0]}\right) = \underset{(12)}{49(\text{CHO})} + \underset{(0.02)}{0.07\sum}\text{PAR} + \underset{(8200)}{\frac{16600}{T}} - \underset{(30)}{62} \qquad n = 16, r^2 = 0.65, \tag{3}$$

where (CHO) is the proportion of aldehyde functional groups in the DOM; $\sum$PAR is the cumulative photosynthetically active radiation experienced by the sample (W/m^2), and T is the cumulative temperature (K). Only those variables significant at the 95% probability of not being zero are included, and the numbers in the brackets are the standard errors in the coefficient and the constant term. Specific rates were used as they take the initial concentration of DOC into account, which was found to be significant in equation (2).

Only one compositional measure of the DOM was found to be significant at any time and the one that gave the highest proportion of variance explained was the proportion of aldehyde-C (CHO, Figure 4). However, two other significant models were possible although in both cases the proportion of variance explained decreased. The two alternative models were based upon carboxyl-C (r^2 = 0.59) and N-alkyl (r^2 = 0.49). In the latter case N-alkyl was negatively correlated with the rate (Figure 4).

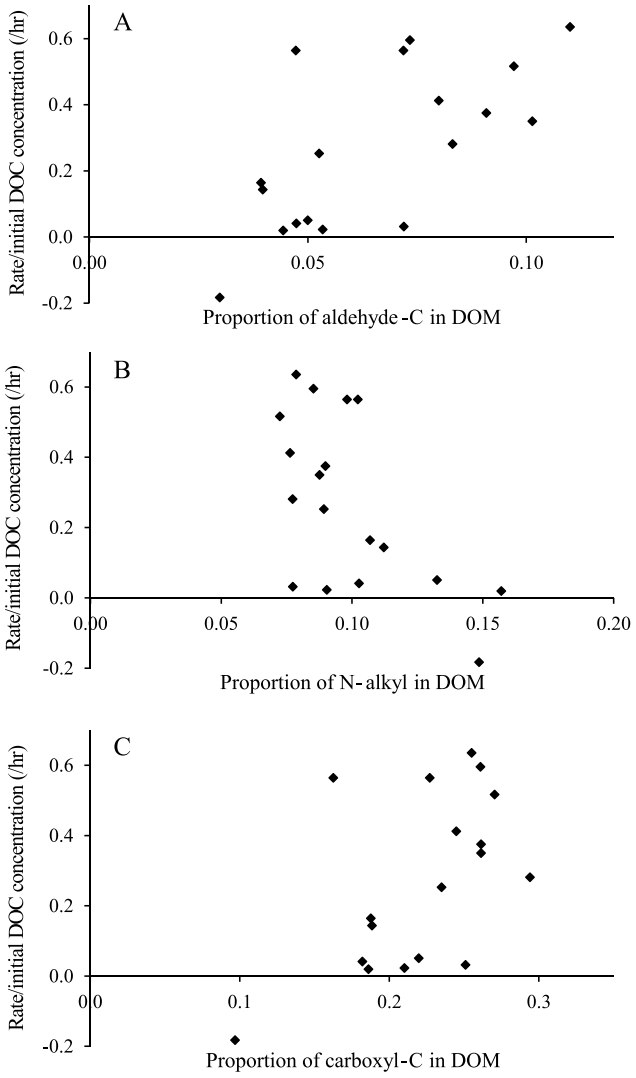

Figure 4. The comparison of the specific initial rate (per hour) to the proportion of (a) aldehyde-C, (b) N-alkyl C, and (c) carboxyl-C.

As the reciprocal of absolute temperature was significant in the regression equation (equation (3)), it was possible to estimate the activation energy of the degradation to be 11 ± 6 kJ/g C. This is higher than the value found by *Moody et al.* [2013] of 2.6 ± 1.2 kJ/g C. It is difficult to find studies that measure activation energy in comparative systems, but *Alperin et al.* [1994] give a value of 6.7 kJ/g C for DOC in marine sediments.

The significant term in ∑PAR in equation (3) suggests that it would be appropriate to calculate apparent quantum yield (AQY) for the photo-induced loss of DOC as 7.1 mmol C/mol photons with a range of −8 to 89 mmol C/mol photons. *Moody and Worrall* [2016] estimated AQY for photo-induced DOC loss to be between 82 and −56 mmol C/mol photons; this range is much larger than the range found in *Moody et al.* [2013] of 9.6 to −1.7 mmol C/mol photons, and the literature values cited therein [*Osburn et al.*, 2009]. Note that in all cases some photo-production was measured on some occasions.

When the data are plotted against the proportion of aldehyde-C, then it is possible to interpret the data as belong to two groups (Figure 4). One group is marked by low rates of degradation with $\frac{\text{rate}}{[DOC_0]}$ between −0.18 and 0.25 per hour, while the second group 0.28 to 0.68 per hour and when divided in this manner, there was a significant difference in the aldehyde proportions of the two groups (one-way ANOVA $p < 0.01$; group 1 mean 0.05 and group 2 mean 0.08) and a significant difference in the specific rate (one-way ANOVA $p < 0.01$; group 1 mean 0.06 per hour and group 2 mean 0.48 per hour). Logistic regression analysis was then used to understand what controls the difference between these groups and the best fit equation was

$$\log_e\left(\frac{\theta}{1-\theta}\right) = \underset{(55)}{130}(\text{CHO}) - \underset{(3)}{8} \qquad n = 16, r^2 = 0.59, \tag{4}$$

where θ is the probability of result being in group 2. Only those variables found to be significant at the 95% probability of not being zero were included, and the numbers in brackets refer to the standard errors in the coefficient or constant terms. Equation (4) means that for a greater than 50% probability of being in group 2 the following inequality has to be met:

$$(\text{CHO}) > 0.06. \tag{5}$$

Table 3. The Removal Proportion of the Fluvial Organic Carbon as Modeled With and Without the Proposed Selection Rule for the Rate Constants of the Model for Fluvial Organic Carbon Turnover Proposed by *Worrall and Moody* [2014]

	Removal Rate (%)	
	Without Selection Rule	With Selection Rule
DOC	69 (67–72)	67 (62–74)
POC	37 (32–43)	22 (21.7–22.5)
TOC (POC + DOC)	57 (53–59)	50 (47–54)

To discover if any hydroclimatic variables were controlling the aldehyde content of the DOM, each hydroclimatic variable was regressed against the aldehyde content. The r^2 of these regressions showed that the discharge 17 h, and the rainfall volume 20 h, before the sample was collected had the most influence on the aldehyde content (aldehyde proportion = 0.02 [discharge 17 h before] + 0.06, $r^2 = 0.32$; aldehyde proportion = 0.01 [rainfall volume 20 h before] + 0.06, $r^2 = 0.32$). As both relationships were positive, this showed that with higher rainfall and higher stream discharge before the sampling occasion there was a higher proportion of aldehyde carbon in the DOM.

When hydroclimatic variables were considered to model the rate of DOC degradation, then only one variable was found to be significant and when included no compositional measures were also significant:

$$\left(\frac{\text{rate}}{[\text{DOC}_0]}\right) = \underset{(0.03)}{0.07}Q_{t-12} + \underset{(0.05)}{0.15} \qquad n = 16, r^2 = 0.36, \tag{6}$$

where $Q_{t\text{-}12}$ is the discharge 12 h before the start of the degradation experiment (m^3/s) and the numbers in the brackets below the equation represent the standard error in the coefficient and constant terms. An examination of the flow data shows that the timescale of the hydrograph within the study catchment is of the order of 4 h, i.e., a relatively high flow 12 h prior to the experiment means that the experiment was being conducted at time of base flow or on the recession limb of an event. Visual inspection of flow 24 h either side of each degradation experiment suggested that the fastest degradation rates occurred, while the flow was still decreasing after an event, rather than during a period of steady base flow. The slowest degradation rates, and the times of net DOC production, occurred on the highest flows.

Given the above results, it was possible to alter the model of *Worrall and Moody* [2014] to include a selection rule as to which set of rate constants to use under which circumstances. On the basis of the above results, the rate constants for the model were divided into two groups with the group with high-magnitude rate constants being selected when the flow from the catchment was less than the 50th percentile flow (median flow) and the low-magnitude rate constants (including the possibility of net production of DOC) were selected when flow was greater than the median flow for the catchment. When the rate constant selection rule was included in the modeling, then the rate of DOC removal decreased slightly (Table 3), but the rate gave a far lower rate of POC loss, which means that both the POC and total organic carbon (TOC) removal rates were lower than when no selection rule was included. The reason for this is that the new rule means the fastest degradation rates occurred at times of lowest flows when less DOC is moving.

4. Discussion

4.1. DOM Characterization

For comparison with the bomb calorimetry values found in this study, the energy budget of the study catchment has been reported by *Worrall et al.* [2015]. The aboveground biomass in the study catchment had a median gross heat value of 19.1 ± 1 *MJ* kg^{-1} (median ± the interquartile range), and the gross heat value of peat soil varied from 19.9 *MJ* kg^{-1} at the surface to a maximum of 21.2 *MJ* kg^{-1} at 1 m depth. The gross heat values of the DOM samples were much lower than the values of the standards and reported values of other organic materials present in the ecosystem and are indicative of DOM being highly oxidized organic matter [*Masiello et al.*, 2008].

In their review, *Worrall et al.* [2013] found two studies from which an OR for DOM from rivers or lakes could be calculated (OR = 0.87 and 0.95) [*Martin et al.*, 2006; *Davis et al.*, 1999], i.e., very similar to the highly oxidized material found in this study (Table 2).

Baldock et al. [2004] showed the results of ^{13}C NMR on carbohydrate, protein, lignin, lipid, carbonyl, and char, as model components for modeling cycling and composition of organic matter, and comparing these results to the NMR results of this study showed that none of those model components have relative intensities similar to DOM. This implies that the DOM in this study does not have a structure similar to carbohydrate, protein, lignin, lipid, carbonyl, or char but is likely to be a mixture of these molecules.

4.2. DOC Degradation

The loss of DOC over 70 h was a similar total loss to that found by *Moody and Worrall* [2016] in experiments conducted by the same method. Similar to that study, the majority of the DOC loss occurred in the first few hours of the experiment, with, on average, 21.2 mg C/L lost in the first 7 h (53% of initial DOC) and 7.6 mg C/L lost in the remaining 63 h (19% of initial DOC).The rates of DOC degradation recorded by *Graneli et al*. [1996] of 0.0009 to 0.4 mg C/L/d were much lower than those in this study but were from water with a lower initial DOC concentration (3.9 to 19.4 mg C/L). As the rate of degradation is linked to the DOC concentration [*del Giorgio and Pace*, 2008; *Moody et al*., 2013], it is not surprising that river with a lower initial concentration would have lower rates of degradation. The rate of DOC concentration change in the ambient conditions in the degradation experiments (68% loss of DOC) is similar to the total losses found by other studies. *Jones et al*. [2016] measured an average DOC loss of 43% from filtered peatland waters, whereas *Gennings et al*. [2001] found 72% TOC loss (in headwater streams where the POC content was very low). The large concentrations of DOC found in the study stream suggest that the DOM is young and highly degradable and that studies conducted farther downstream in catchments would be studying relatively old and reacted DOM.

The results found by this study provide an estimate of rates and DOC losses from an upland system; however, they do not take into account the hydrological complexity of the natural system, such as dilution from additional water input. However, the lack of any significant seasonal differences in the DOM composition or DOC concentration (both initial and changes) is interesting as it suggests that variability in weather at the site is not the main factor controlling the degradability of DOM. The specific rate of DOC change was best modeled using two environmental variables in addition to the aldehyde proportion: the total PAR and air temperatures that the water samples were exposed to during the degradation experiments. The significance of these environmental factors suggest that the weather the DOM is exposed to once it is in the water is more relevant to its degradation rate than the weather conditions under which the DOM was generated (in the peatland). Regression analyses of the degradation rates of DOC with the environmental conditions (air and soil temperature, and rainfall) from the field site in the 7 days and 24 h preceding sampling did not find significant models; however, there was a significant relationship between the aldehyde proportion and rainfall. The relationships between aldehyde proportion and discharge (both 17 and 12 h before sampling) and rainfall were positive, showing that with higher rainfall and higher stream discharge before sampling, there was a higher proportion of aldehyde carbon in the DOM and therefore had higher rates of DOC loss.

The study has shown that DOM is highly oxidized relative to other components in the peat ecosystem. The gross heat, C_{ox}, and OR values of the DOM are more oxidized than the vegetation and soils components from which the DOM must have been derived [*Martin et al*., 2006; *Davis et al*., 1999]. *Worrall et al*. [2016] have proposed that DOM is the intermediary between soil, or litter, and CO_2 rather than a by-product of the oxidation of naturally occurring organic matter, i.e., as NOM is oxidized it can become soluble. If DOM is an intermediary between soil and litter and CO_2, then it suggests that the longer between flushing events the more oxidized the DOM will become.

The importance of aldehyde functionality in controlling the rate of degradation can be readily explained if the process of DOM turnover is considered as dominated by oxidation processes. The study found that the effect of increased aldehyde functionality is colinear with increased carboxylic acid functionality and decreased N-alkyl groups (Figure 3). Aldehyde groups are readily oxidized to carboxylic acids and carboxylic acids are readily oxidized to CO_2 as components of the Krebs cycle [*Thauer*, 1988]. At the pH present in the stream water of this catchment (pH 4.36) the carboxylic acids may not be charged, whereas the N-alkyl groups may well be protonated [*Oliver et al*., 1983]. It is hypothesized that in these circumstances the solubility of the DOM is being controlled by amino groups and not by carboxylic acid groups. The enhanced solubility and the positive charge may limit the capacity of DOM to be metabolized, while the highly oxidized groups are readily taken into to established metabolic pathways. The importance of oxidized groups over nutrient-rich groups suggests that the processing of DOM in these first-order, peat-hosted streams is as an energy

source and not as a nutrient source. In these first-order streams the N source might well be ammonium and not dissolved organic nitrogen. This hypothesized explanation means that processing of DOM may change rapidly as pH increases in the higher-order streams: at higher stream pH the amino groups may not be protonated; rather, it is the carboxylic acids that will be controlling solubility.

5. Conclusion

The study showed that the DOC concentration change in the first hour ranged between +5.27 and −37.05 mg C/L or assuming a first-order rate then −0.18 to 0.64 per hour, i.e., although degradation dominated net production was also observed. The rate of degradation had a small activation energy (11 ± 6 kJ/g C) and apparent quantum yields between −8 and 89 mmol C/mol photons. There was a significant role for composition of the DOM and degradation increased with an increased proportion of aldehyde or carboxylic acid functional groups in the DOM or decreased with increased proportion of N-alkyl groups. The degradation rates could be divided into two groups with the fastest rates occurring at times of base flow or at least related to the stream discharge 12 h before the rate measurement—this would mean degradation rates were on the recession limb of the hydrograph. Including the results into modeling of the fate of fluvial organic carbon predicted that the annual removal rate of DOC across and 818 km^2 catchment was 67% and 50% for TOC.

Acknowledgments
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